

## Effect of pH on the removal of arsenic and antimony using reverse osmosis membranes

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### Abstract

Increasing attention has been focused on the health effects associated with ingestion of low levels of arsenic and antimony in drinking water. Accordingly, this study was conducted in order to identify the effect of solution pH on the removal efficiency of arsenic and antimony for drinking water using recently developed RO membranes. In this study it was found that the removals of As(V) and Sb(V) are much higher than those of As(III) and Sb(III) over all investigated pH levels (pH 3–10). The removal of arsenic compounds was strongly affected by the solution pH, especially As(III), whereas the removal of antimony compounds shows no dependence on the solution pH since the oxidation state of antimony changes from Sb(III) to Sb(V) within very short periods of time. It was demonstrated that pH control for the membrane feed water is more essential for the successful removal of arsenic compounds than the case of antimony compounds. Consequently, it is assumed that the removal of antimony in drinking water by RO membranes has a higher efficiency than that of arsenic compounds, regardless of pH changes.

*Keywords:* Arsenic; Antimony; Reverse osmosis membrane; Solution pH

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### 1. Introduction

The toxicity of arsenic in humans at a low dose is well known [1]. Many countries such as India, Bangladesh and China have reported serious health hazards from arsenic in drinking water. Chronic health effects from consuming arsenic-contaminated drinking water are delayed.

Skin lesions are generally first and appear after a minimum exposure of approximately 5 years. Chemical behavior and toxicity of antimony are similar to that of arsenic [2]. Inhalation exposure to antimonials has been reported to produce pneumonitis, fibrosis, bone marrow damage and carcinomas. However, its chemical behavior in aquatic environments is not understood exactly. Both arsenic and antimony commonly exist in different oxidation states: trivalent(III) and

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pentavalent(V). The dominant species of them is a function of pH and redox potential.

Membrane technologies for water treatment have been vastly improved in areas of water flux, salt rejection, and especially in their ability to maintain high performance levels at substantially lower operating pressures than their predecessors. Reverse osmosis (RO) membranes have been identified as one of the best available technologies to reduce hazardous inorganics in water. Accordingly, this research was conducted using a recently developed RO membrane with the following objectives:

- to demonstrate the dependence of the removal of solute on their radius and charge
- to identify the effect of pH on the removal of arsenic and antimony
- to investigate the relationship between the removal different of species of arsenic and antimony.
- to compare antimony behavior with arsenic behavior.

## 2. Theoretical considerations

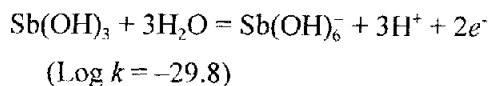
### 2.1. Arsenic chemistry

Arsenic, atomic number 33, is in the group VB of the periodic table, directly below phosphorous. Arsenic is considered metalloid and occurs in a variety of forms and oxidation states. The two oxidation states common in drinking water are arsenate and arsenite. Arsenate is the thermodynamically stable form of inorganic As in oxic water, and generally predominates in surface water. The chemical equilibrium of arsenic compounds is shown in Fig. 1. Both arsenite and arsenate occur in several protonate forms; at near-neutral pH, the predominant species are  $\text{H}_3\text{AsO}_3$  for arsenite and  $\text{H}_2\text{AsO}_4^-$ , and  $\text{HAsO}_4^{2-}$  for arsenate. This means that arsenate exists as an anion at typical pH (5–8) in natural water, while arsenite remains as a neutral molecule at the same pH region. Arsenite is

proposed to have one negative charge at a pH over 9.2.

### 2.2. Antimony chemistry

So far, precise molecular structures and physical and chemical parameters are found in the literature only for Sb(V) oxide [3]. The antimony pentoxide is easily soluble in water and aqueous solutions by forming  $\text{SbO}_3^-$ , which is present as  $\text{Sb}(\text{OH})_6^-$ . Antimony trioxide has a limited solubility in aqueous solutions (<5 mg/L). In solutions of pH from 2 to 10.4, the solubility of  $\text{Sb}_2\text{O}_3$  is independent of the pH, which indicates the formation of an undissociated substance, i.e. meta-antimonious acid ( $\text{H}_3\text{SbO}_3$ ) or better antimony hydroxide ( $\text{Sb}(\text{OH})_3$ ). More alkaline solutions dissolve the oxide as antimonite ions ( $\text{H}_2\text{SbO}_3^-$  or  $\text{Sb}(\text{OH})_4^-$ ). Therefore, Sb(III) exists as a neutral molecule at the comprehensive region of pH. The chemical equilibrium of antimony compounds is shown in Fig. 2. On the other hand, the antimony equilibrium is also thought to be controlled by the following equation:



This equation shows a concentration ratio of Sb(V) in the form of  $\text{Sb}(\text{OH})_6^-$  to Sb(III) in the form of  $\text{Sb}(\text{OH})_3$  to be  $10^{18.4}$  in well aerated oxic water at pH 7. Hence, Sb(V) should be the dominant and only detectable species in oxic water.

## 3. Experiment

### 3.1. Reverse osmosis experiments

Two types of RO membranes, ES-10 and NTR-729HF, produced by the Nitto Electric Industrial Co. (Japan), were used in this research.

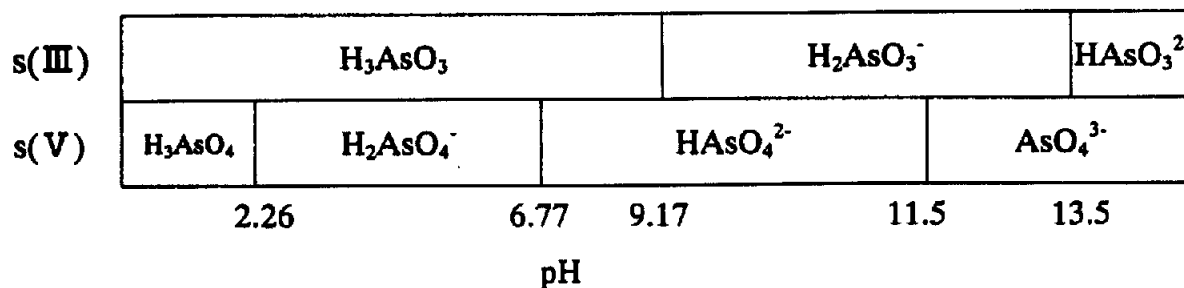


Fig. 1. Schematic diagram of chemical equilibrium of the arsenic compounds.

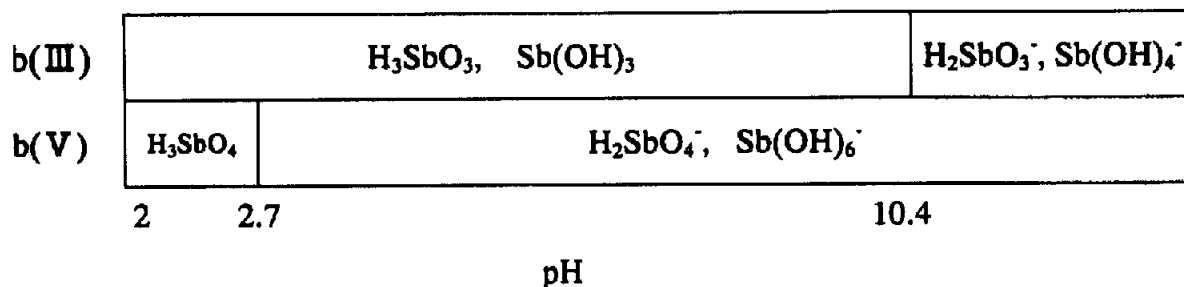


Fig. 2. Schematic diagram of chemical equilibrium of the antimony compounds.

is assumed that these membranes have a negative charge because their skin layers are made of polyamide (ES-10) or polyvinyl alcohol (TR-729HF). Nominal removal of sodium chloride by ES-10 and NTR-729HF at 1.5 MPa with 0.15% is 99.6% and 93.0%, respectively. The experiments of RO membranes were carried out at laboratory scale in batch style. The membrane module used in this research was a flat-sheet type (C40-B, Nitto Electric Industrial Co.) with an effective membrane surface area of 1.2 cm<sup>2</sup>.

## 2. Chemicals and analytical methods

All chemicals used were of analytical-reagent grade or higher purity. For the research, the composition of the feed solution of neutral, cation, arsenic and antimony were prepared as shown in Table 1. A relatively high concentration

Table 1  
Composition of feed solution

Performance	Composition	Concentration
Anion removal	Ethyl alcohol	100 mg, TOC/L
	Isopropyl alcohol	100 mg, TOC/L
	n-butyl alcohol	100 mg, TOC/L
	NaCl	50 mg, Cl/L
	MgSO <sub>4</sub>	50 mg, SO <sub>4</sub> /L
Arsenic removal	As <sub>2</sub> O <sub>3</sub>	50 µg, As/L
	Na <sub>2</sub> HAsO <sub>4</sub> ·7H <sub>2</sub> O	50 µg, As/L
	Sb <sub>2</sub> O <sub>3</sub>	10 µg, Sb/L
	KSb(OH) <sub>6</sub>	10 µg, Sb/L
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of neutral and anionic solutions was initially selected in order to investigate the relationship between neutral and anionic solute by RO

membranes. Standard stock solutions for As(III) and As(V) were prepared by dissolving  $As_2O_3$  and  $Na_2HAsO_4 \cdot 7H_2O$  in distilled water. The required pHs for anionic and arsenic feed water were adjusted with NaOH and  $HNO_3$  at 3, 5, 7 and 10, respectively.

A stock solution for Sb(III) was prepared by dissolving the appropriate amount of  $Sb_2O_3$  in distilled water. The resulting solution was filtered through a 0.45- $\mu m$  filter. A stock solution containing Sb(V) was prepared using  $KSb(OH)_6$ . The required pHs were adjusted with NaOH and  $HNO_3$  at 3, 5, 7 and 10, respectively. An ion chromatography, TOC analyzer, hydride generation, inductively coupled plasma atomic emission spectrometer (HG-ICP-AES) and inductively coupled plasma mass spectrometer (ICP-MS) were used for the measurement of anions, neutral solutes, arsenic and antimony, respectively.

## 4. Results and discussion

### 4.1. Comparison of removal and flux using NaCl

The evaluation of removal efficiency between two types of membranes used in this study was carried out with 500 mg-NaCl/L at 0.75 MPa. The comparison for removal and flux is shown in Fig. 3. Permeate flux was relatively low for the NTR-729HF compared to the ES-10. ES-10 has a higher flux,  $1.14 \times 10^{-6}$  m/s, than NTR-729HF,  $0.95 \times 10^{-6}$  m/s. In addition, the removal of NaCl by ES-10 was more than 97%, while the removal by NTR-729HF was 89%. Considering removal and flux characteristics, ES-10 has better results than NTR-729HF.

### 4.2. Dependence of the removal of solutes on their radius and charge

In order to identify the dependence of the removal of solutes on their radius and change, the evaluation was carried out with three kinds of neutral solutes and two kinds of anionic solutes.

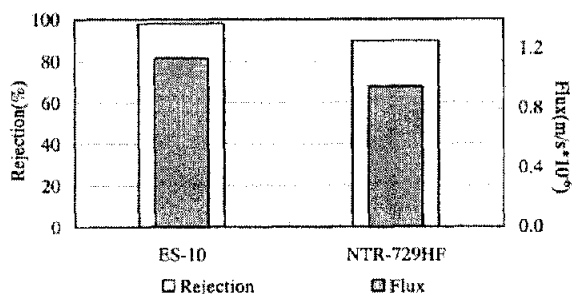


Fig. 3. Comparison of rejection with flux (with 500 mg NaCl/L, 0.75 MPa).

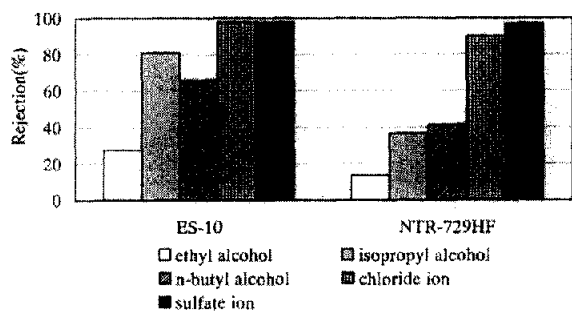


Fig. 4. Dependence of the removal of solutes on their radius and charge.

Ethyl alcohol, isopropyl alcohol and n-butyl alcohol were chosen as neutral solutes and chloride and sulfate ions were chosen as anionic solutes. The stoke radii of ethyl alcohol, isopropyl alcohol, n-butyl alcohol, chloride and sulfate ions are 0.198, 0.240, 0.258, 0.120 and 0.229 nm, respectively. The stoke radii were calculated with the Stokes-Einstein equation ( $r_s = kT/6\pi\mu D_s$ ) from literature diffusivities in dilute aqueous solution [4]. Fig. 4 shows the results at neutral and ionic solutes. The removal of ionic solutes is higher than that of neutral solutes, despite their having radii smaller than those of neutral solutes. The removal of neutral solutes by ES-10 and NTR-729HF was lower than 65.9%, while the removal of ionic solutes by these membranes was higher than 90%. In the

case of sulfate ion, the removal was the highest value — 98% and 97% — than any other. Fig. 4 also shows that the larger the stoke radius of neutral solutes, the higher the removal. From this result it was demonstrated that the removal of neutral solutes shows dependence on the radius, whereas the removal of anionic solutes does not.

#### 4.3. Effect of solution pH on anionic removal

Fig. 5 gives the results of the two types of RO membranes for removing anions such as chloride and sulfate in the dilute solution as a function of solution pH. The removal of chloride ion by ES-10 was 98% except the case of pH at 3. In the case of NTR-729HF, the removal of chloride ions was 90% except at pH 3. These results show that the removal of chloride ions using RO membranes was affected by solution pH, especially at a lower range of pH, whereas the removal of sulfate ions with RO membranes was also high, regardless of pH range. The removal of sulfate ions with these membranes was more than 94%. The sulfate ions were in divalent ion form through all the pHs investigated. The removal of sulfate ions was higher than that of chloride ions for both types of RO membranes. The RO membranes used in this study are negatively charged through all the pH range investigated. The effective charge density decreases with the decrease of pH because the isoelectric point of these membranes is located at a lower pH region. Consequently, the decrease of chloride removal at lower pH is due to the decrease of the effective charge density of these membranes.

#### 4.4. Effect of solution pH on the removal of arsenic compounds

The removal of arsenic compounds at different pHs is shown in Fig. 6. The removal of arsenate was higher than that of arsenite over the pH range of 3 to 10 investigated in this study. The removal of arsenic compounds is almost

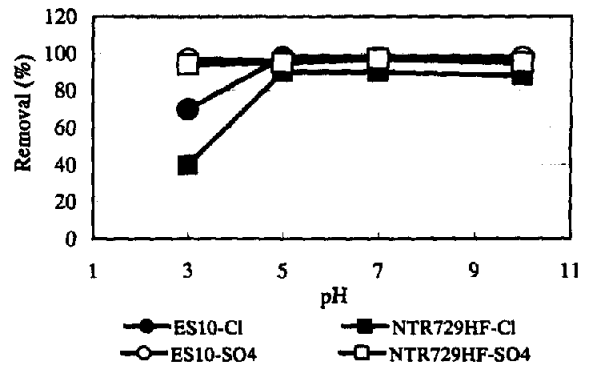


Fig. 5. Effect of solution pH on anion removal.

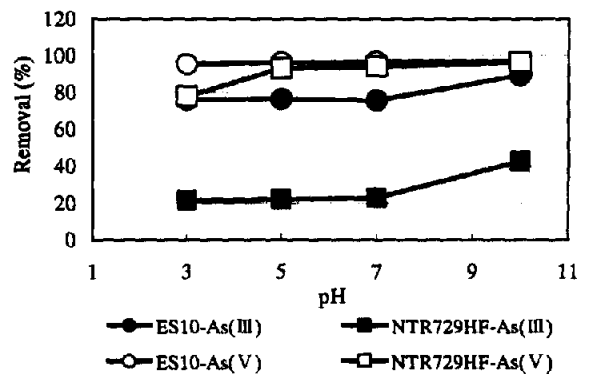


Fig. 6. Effect of solution pH on the removal of arsenic compounds.

proportional to the removal efficiency of sodium chloride. The removal of arsenite by ES-10 was more than 75% through all the pH range investigated, while the removal by NTR-729HF was lower than 43%. The removal of arsenite was increased sharply as the pH increased from 7 to 10. It shows that the effect of solution pH affects the removal of arsenite because most of the arsenite exists in monovalent anion form at pH 10, while most of the arsenite exists in a neutral molecule at pH 3, 5 and 7.

The removal of arsenate by ES-10 was more than 95% through all the pH range investigated.

In the case of NTR-729HF, the removal of arsenate was increased with the increase of pH from 3, 5, 7 and 10. Hence, the results of the experiment show a significant effect of solution pH on the removal of arsenic compounds using RO membranes.

#### 4.5. Effect of solution pH on the removal of antimony compounds

The effect of solution pH on the rejection of antimony compounds by two types of membranes is presented in Fig. 7. The removal of Sb(V) was higher than that of Sb(III) in the range of pH 3–10. This can be explained by the same phenomenon as As(V) because Sb(V) also exists in monovalent or divalent form in the investigated pH ranges, while Sb(III) exists in a neutral molecule. Fig. 7 also shows that both Sb(III) and Sb(V) removal are almost constant over a pH range 3–10 except with case of Sb(III) removal with the NTR-729HF membrane. Sb(III) removal with the NTR-729HF decreased sharply from 60.2% to 45.7% with a reduction of pH from 7 to 10.

Unfortunately, it still remains unclear what is responsible for this phenomenon. Fig. 7 also shows that the removal of antimony compounds used in this research was almost proportional to the removal efficiency of NaCl. When the results

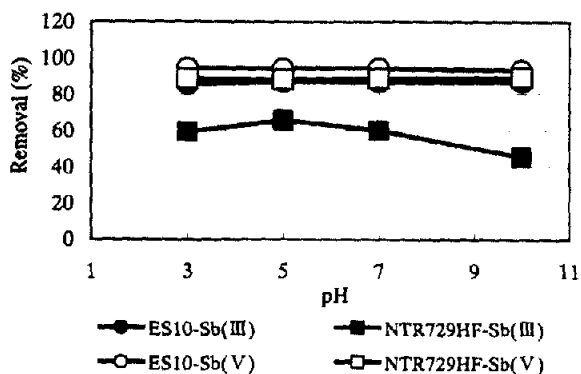


Fig. 7. Effect of solution pH on the removal of antimony compounds.

shown in Fig. 7 are compared to that of Fig. 6, we notice that the removal of Sb(III) is much higher than that of As(III) though they have almost the same form as a neutral form in aqueous solutions. In fact, the oxidation state of antimony changes from Sb(III) to Sb(V) occurred within very short periods of time.

## 5. Conclusions

On the basis of the results of this study, the following conclusions can be drawn. The dependence of the removal of neutral solutes on their stoke radius is high. The larger the stoke radius of neutral solutes, the higher the removal. On the other hand, the removal of anionic solutes shows no dependence on the radius. The removal of arsenic and antimony compounds is almost proportional to the removal efficiency of NaCl. The removal of As(V) and Sb(V) is much higher than As(III) and Sb(III) over the pH range 3–10. The effect of solution pH on the removal of arsenic using RO membranes was strongly affected by the solution pH, especially As(III), whereas the effect of solution pH on the removal of antimony can be negligible. It can be explained that the oxidation state of antimony changes from Sb(III) to Sb(V) within a very short time. Consequently, it was demonstrated that pH control for the membrane feed water is essential for the successful removal of arsenic compounds.

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